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Cadmium Emissions from Pigment and Stabilizer Manufacturing Phase 1. Technical Report

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Cadmium Emissions From Pigment and Stabilizer Manufacturing — Phase I Technical Report

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A technical report on cadmium emissions from pigment and stabilizer manufacturing. Descriptions of these industries and associated air pollution control equipment are presented. Cadmium emissions as well as health risks from exposure to these emissions from all plants in the U.S. are discussed.

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Emission Standards Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park NC 27711

June 1988

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TECHNICAL REPORT:

CADMIUM PIGMENT AND STABILIZER MANUFACTURING

I. DEFINITION OF SOURCE CATEGORIES

A. Pigment Manufacturing

1. Plants in operation. At present there are four plants in the U.S. that produce cadmium pigments: Ciba-Geigy in Glens Falls, New York; H. Kohnstamm & Company in Newark, New Jersey; Harshaw/Filtrol Partnership in Louisville, Kentucky; and SCM Corporation in Baltimore, Maryland.

2. Processes. Cadmium pigments are stable inorganic coloring agents that are produced in a range of brilliant shades of yellow, orange, red, and maroon. The cadmium pigments are based upon the compound cadmium sulfide (CdS), which produces a golden yellow pigment. Partial substitution of cadmium in the crystal lattice by zinc or mercury and substitution of sulfur by selenium form a series of compounds making up the intermediate colors in the lemon-yellow to maroon range of colors. The pigments are fine, discrete particles of colored powder with diameters of about 1 micrometer, which are distributed and suspended in the material to produce a uniformly colored product. Cadmium pigments have excellent heat stability which makes them very useful in high-temperature processing. Cadmium pigments primarily are used in plastics but also are used in some coatings and ceramics.[1]

There are two general types of cadmium pigments produced in the U.S. Pure pigments refer to the CdS or cadmium selenide pigments that typically contain approximately 65 percent cadmium.[2] Chemically pure cadmium yellows and sulfoselenides are used full strength when low pigment loadings are wanted (because less pigment is needed to achieve the desired color) for example, in the manufacture of color concentrates for plastics.[3] Lithopone pigments are pure cadmium pigments that have been diluted with barium sulfate. The average cadmium content of lithopone pigments is approximately 26 percent by weight.[2] Lithopones have only one-half the tinting power of pure pigments; but when high pigment loadings can be tolerated, the lithopones offer tinting strength and hiding power that compare, on an equal cost basis, with chemically pure pigments. The greatest use of the lithopones is in the coloring of plastics with dry blends.[3]

The production of all cadmium pigments is structured around one generic process which is illustrated in Figure 1. However, each of the cadmium pigment manufacturers has developed various proprietary methods for generating pigments with particular color shades and properties. These proprietary modifications involve altering the portions and types of ingredients used, varying the calcination time, and adding or deleting steps such as filtration, washing, drying, blending, and grinding. For the purposes of this report, only the generic cadmium pigment production process and its cadmium emission sources are described. Plant-specific process description data have been provided to EPA by the four plants in question, but these data have all been labeled confidential by the companies, and, therefore, cannot be presented here.

The basic raw materials for the production of cadmium pigments are pure solutions of either cadmium sulfate ($CdSO_4$) or cadmium nitrate. Cadmium sulfate is predominantly used. These materials either are bought in bulk in liquid form or are produced onsite using cadmium metal or cadmium sponge (a porous, high-surface-area form of cadmium metal) and the appropriate acid. The $CdSO_4$ solution is then mixed with variable amounts of an aqueous solution of sodium or other alkali sulfide (depending on the desired color) in a precipitation reactor. This procedure causes CdS to precipitate in crystallographic form. The $CdSO_4$ is reacted with an alkali sulfide-selenide to produce pigments of a red shade (cadmium sulfo-selenides).

Upon completion of the batch process precipitation reaction, the precipitates are filtered from solution, washed, and dried. The dried precipitates are very fine colored particulates; however, they possess no pigment properties at this point. The true colors and properties of the pigments are developed during the calcination or roasting operation. Calcination involves heating the pigment precipitate material in a furnace to a temperature of from 550° to 650°C (1022° to 1202°F). This process converts the pigment material from a cubic to a more stable hexagonal crystalline structure. The calcined pigment material is then washed with hydrochloric acid to remove the remaining soluble cadmium particles. The product of this procedure is again washed with water, filtered, and dried. The final cadmium pigment emerges as a filter cake, which is

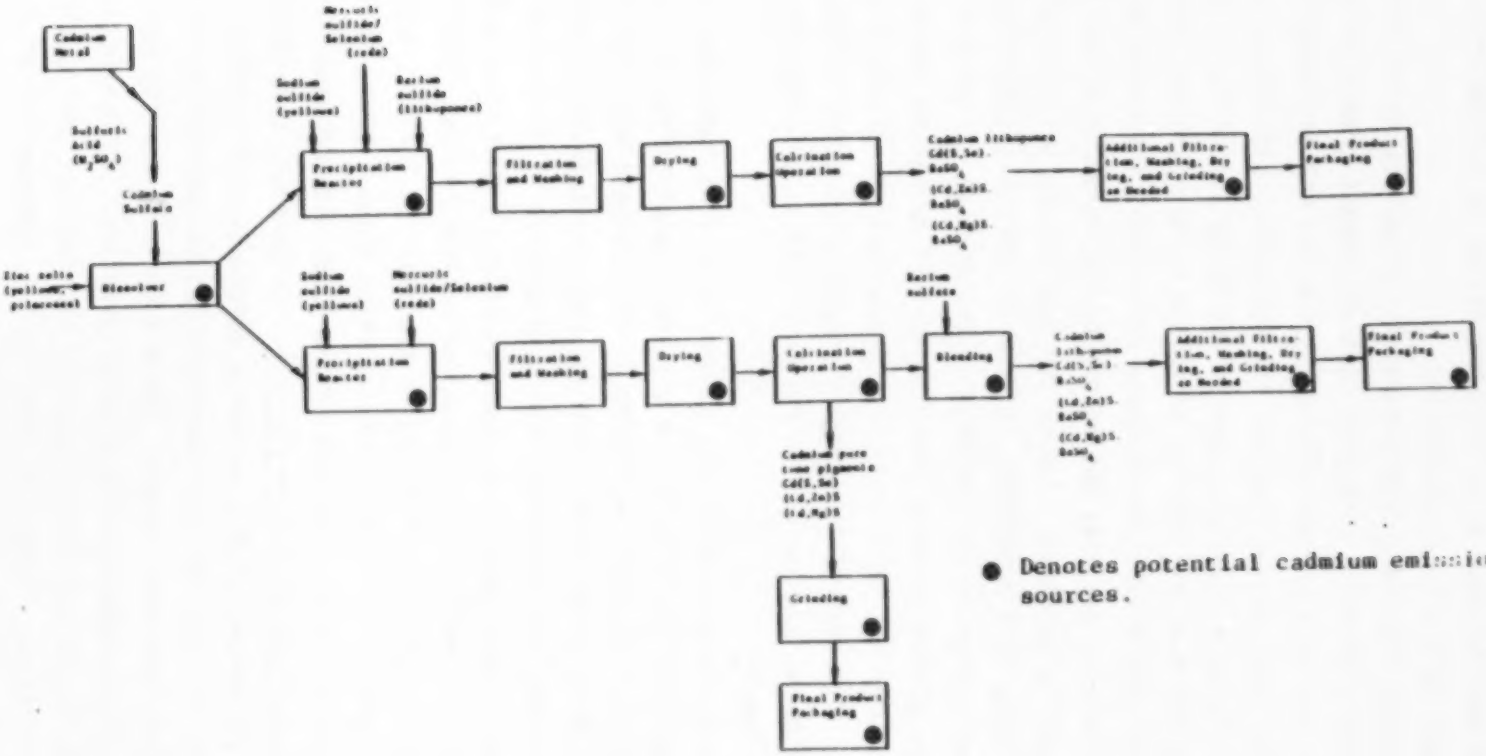

Figure 1. Process flowsheet for the production of cadmium pigments.[1]

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either ground and packaged as a final product or is further processed (e.g., blended) before final packaging.

The process just described predominantly applies to the production of pure cadmium pigments. Lithopone cadmium pigment production can be incorporated into this overall process by the two methods shown in Figure 1. The first method involves the mechanical blending of barium sulfate with the pure cadmium pigment produced by calcining. The similar particle size and specific gravity of barium sulfate and the cadmium pigment enhance the mixability of these compounds. The second method of lithopone production involves adding the barium compound before the pigment mixture is calcined. A more thorough and efficient pigment mixing is achieved using this procedure. Barium is typically added to the precipitation reactor in this process in the form of barium sulfide. Some of the sodium sulfide normally used is replaced by the barium sulfide. Upon reaction with the $CdSO_4$ solution, barium sulfate is coprecipitated with the CdS. The rest of the cadmium pigment production process proceeds as described above, and the entire coprecipitate is calcined and further processed as needed.

Cadmium pigment products are generally sold as homogenous powders with a typical particle size of 1 micrometer (ranging from 0.1 to 3.5 micrometers). However, depending on the ultimate application, they can be supplied in other forms. For the plastics industry, cadmium pigments are sometimes processed into predispersed forms such as master batch pellets. These pellets are cadmium pigments that have been incorporated or dispersed into compounded polymer resins. Other forms in which cadmium pigments are supplied to the plastics industry are paste concentrates and liquid colors, both of which allow pigment to be added to plastic resins at different stages of the production process.

3. Projections of industry growth. In general, cadmium pigments account for 25 percent of the worldwide consumption of cadmium. Hydrated ferric oxides and lead and zinc chromates can be substituted in yellow color range applications; however, these materials lack the heat stability important in high-temperature molding of plastics. In the red color range, ferric oxides can substituted for cadmium, but the resulting colors lack high brilliance. Demand in 1983 for U.S. consumption of cadmium for

pigments was 600 metric tons. The projected consumption in 2000 is 700 metric tons.[4] No new plants are expected because existing facilities that are currently operating at less than 100 percent of capacity are expected to be able to meet future demand.

B. Stabilizer Manufacturing

1. Plants in operation. Barium/cadmium stabilizers, also called organo-cadmium soaps, are salts of long chain fatty acids. They can be used as liquids containing 1 to 4 percent cadmium or as powders containing 7 to 15 percent cadmium. At present, there are five plants in the U.S. that produce liquid and/or powdered cadmium stabilizers: Ferro Corporation in Bedford, Ohio; Interstab Chemicals in New Brunswick, New Jersey; R. T. Vanderbilt Chemical Company in Bethel, Connecticut; Synthetic Products in Cleveland, Ohio; and Witco Chemical Corporation in Brooklyn, New York.

2. Processes. Cadmium-containing stabilizers are used to retard polymer degradation that occurs in polyvinylchloride (PVC) when it is exposed to heat and ultraviolet light. Cadmium-based stabilizers are usually mixed with barium salts to make highly effective, long-life stabilizers that have no adverse effect on the processing of PVC products and do not change the properties of the products during service. Cadmium/zinc stabilizers work in a similar manner to barium/cadmium stabilizers but are not as effective in maintaining color and clarity and are not as long lasting.[5] Commercial barium/cadmium stabilizers are produced in liquid and solid forms.

The stabilizer production process can be highly variable because many of the stabilizers produced are custom blended for specific applications. Liquid stabilizers are prepared by dissolving CdO in a heated solution of the relevant organic acid and an inert organic solvent. Following the slow acid-base reaction, the water produced is driven off by heating. The product is filtered, and the solution of the cadmium soap is packaged in drums for sale.[6]

Figure 2 is a simplified flow diagram for powdered stabilizer production. Powdered stabilizers are produced by reacting the relevant organic acid with caustic soda to make a soluble sodium soap. A solution of cadmium chloride is prepared by dissolving cadmium metal or CdO in

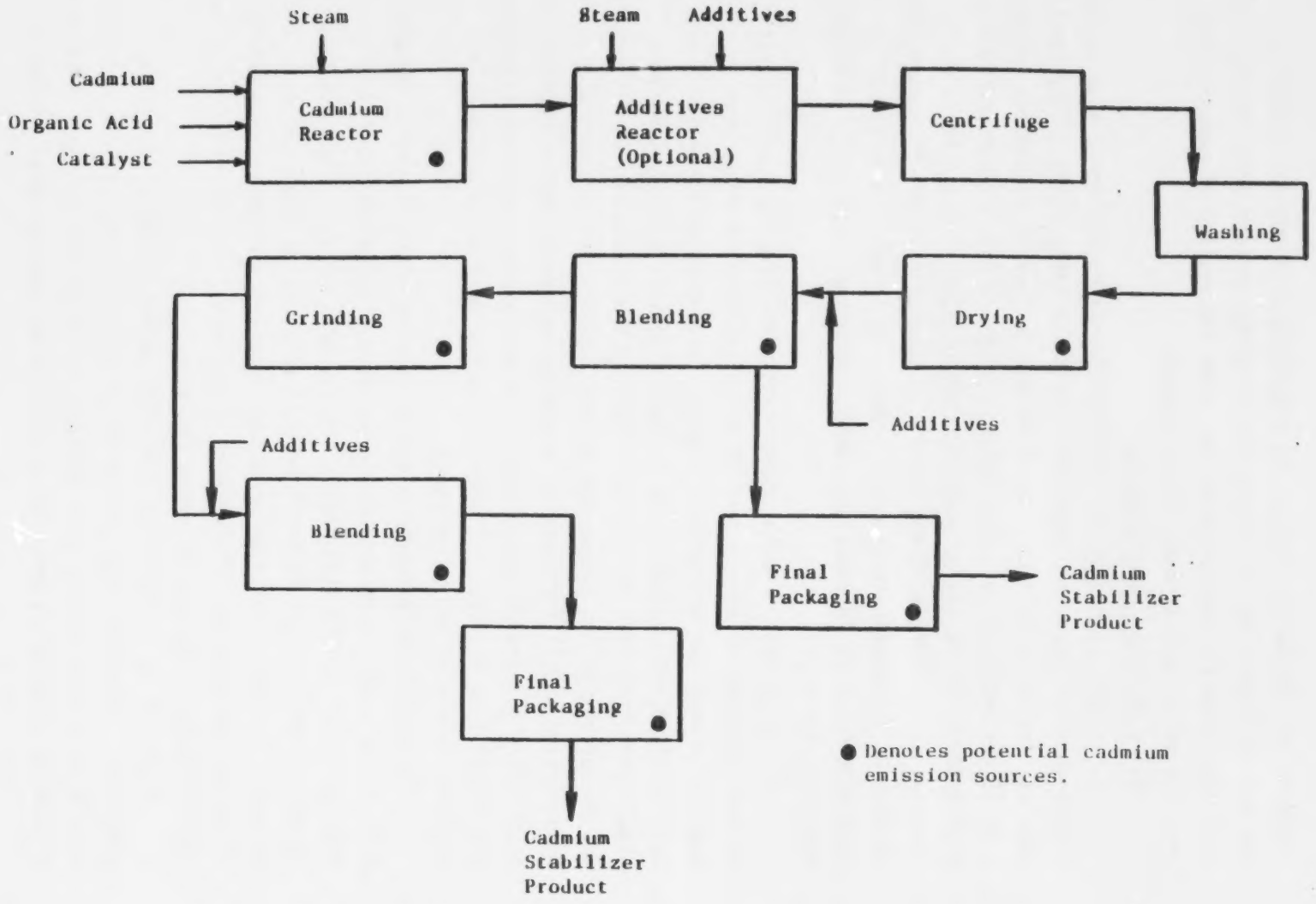

Figure 2. General flowsheet for the production of powdered cadmium stabilizers.[2]

acid. The sodium salt of the organic acid is added to the cadmium chloride solution at an elevated temperature to precipitate the cadmium soap. The resulting slurry is dewatered, and the solid stabilizer product is washed, dried, possibly blended, and packaged.[6] After the basic cadmium stabilizer has been produced, additives and moistening agents may be combined with the soap to create the product required by specific customers. The number and sequence of grinding, blending, and packaging operations that are performed vary depending on the exact product to be made.[6]

3. Projections of industry growth. As plastic stabilizers, organotin compounds are the most efficient, but cadmium compounds are preferred due to their lower cost. Lead stabilizers are relatively inexpensive and effective, but their toxicity and vulnerability to staining by sulfides in the air are major disadvantages.[4] The 1983 demand for cadmium use in stabilizers was 560 metric tons. The projection for 2000 is 800 metric tons.[4] No new plants are expected because existing facilities are currently operating at less than 100 percent of capacity and are expected to be able to produce the additional stabilizers needed to meet demand.

II. EMISSIONS AND CONTROLS

The emission estimates and corresponding risk and cancer incidence for each source in each source category are based on the best available information. In many cases, test data were not available, and emission estimates were generated by plant personnel. In other cases, test data from one plant were used to generate an emission factor for use on similar equipment at other plants. The factors that contributed the most uncertainty to the estimates were the determination of the actual hours per year of operation of the control equipment (due to the batch nature of most of the processes and several batch processes ducted to a single control device) and the cadmium content of the material being processed (due to the large number of products with differing cadmium contents produced in each piece of equipment). Although the source test program helped to reduce the uncertainty of the emission estimates at the pigment plants, a more extensive test program would be needed to remove all

TABLE 1. CADMIUM EMISSION ESTIMATES FOR PIGMENT AND STABILIZER PLANTS

Category/plant	Cadmium emissions, Mg/yr
Pigment Manufacturing	
Ciba-Geigy, Glens Falls, N.Y.	0.69
H. Kohnstamm, Newark, N.J.	0.024
Harshaw/Filtrol, Louisville, Ky.	0.19
SCM Corp., Baltimore, Md.	0.039
Total	0.94
Stabilizer Manufacturing	
Ferro Corp., Bedford, Ohio	0.0032
Interstab Chemicals, New Brunswick, N.J.	0.0054
R. T. Vanderbilt, Bethel, Conn.	0.0084
Synthetic Products, Cleveland, Ohio	0.042
Witco Chemical Corp., Brooklyn, N.Y.	0.032
Total	0.091

uncertainty from these estimates. Table 1 presents the emission estimates for each pigment and stabilizer plant.

A. Pigment Manufacturing

It is estimated that 0.94 megagram (Mg) of cadmium as CdS is emitted annually from the four plants. The emission estimate for each source at each plant was based primarily on information provided by plants in current and previous Section 114 responses and EPA source tests at two plants. Ciba-Geigy provided emission rates for each source based on test data from the same or similar equipment. Emission rates along with typical annual operating hours per year for each process unit or control device and the cadmium content of the material processed were used to calculate annual emissions. In cases where test data or emission factors were unavailable for a process unit controlled by a baghouse, the annual amount of dust collected by the baghouse, the baghouse design efficiency, and the cadmium content of the collected dust were used to estimate cadmium emissions.

Reactor charging for $CdSO_4$ production is uncontrolled at three plants and is controlled by a low-energy wet scrubber at Harshaw/Filtrol. Calcining operations at all four plants are controlled by wet scrubbers. Drying operations are uncontrolled at three plants and controlled by a low-energy wet scrubber at Harshaw/Filtrol. Grinding, blending, and packaging operations are typically controlled by baghouses at each of the four plants. Fugitive emissions that occur inside buildings during the handling and transfer of cadmium-containing materials are typically captured by hooding and eventually ducted to a control device.

B. Stabilizer Manufacturing

It is estimated that 0.09 Mg of cadmium as barium/cadmium stearate and CdO is emitted annually from the five plants. The emission estimate for each source at each plant was based primarily on Section 114 responses and test data provided by the plants. An emission factor for CdO charging to a reactor developed from Interstab Chemicals test data was used to estimate these emissions at the other stabilizer plants. The same mass balance procedure discussed above for processes controlled by baghouses was used on stabilizer sources for which data were unavailable.

The only potential particulate cadmium emission source from liquid stabilizer production is the charging of powdered CdO to the organic acid solution. This process is uncontrolled at one plant and controlled by wet scrubbers at all the other plants. Potential emission sources during powdered stabilizer production include CdO production (only at one plant); charging CdO to the reactor; and drying, blending, and packaging of the final product. The one CdO production process is controlled by a baghouse. Drying operations are typically uncontrolled. Blending and packaging operations are controlled by baghouses at all five plants.

III. PUBLIC HEALTH RISKS

A. Background

Risk assessment is the process used by EPA to develop quantitative estimates of public health risks associated with individual and population exposure to a hazardous or toxic air pollutant. The resultant estimates are considered by EPA to be rough but plausible upper-bound approximations of the risks. Two measures of risk are calculated. One is maximum individual risk and the other is aggregate risk. Maximum individual risk is an estimate of the probability of contracting cancer experienced by the person or persons exposed to the highest predicted annual average concentration of the pollutant. Aggregate risk is an estimate of the increased number of cancer cases for the entire population after 70 years of continuous exposure. It is expressed in terms of annual incidence or number of cancer cases per year.

The estimates are calculated by coupling a numerical constant that defines the statistical exposure-risk relationship for a particular hazardous pollutant with estimates of public exposure to the pollutant. The numerical constant used by EPA in its analysis of carcinogens is called a unit risk factor. It represents an estimate of the increase in cancer risk occurring to a hypothetical individual exposed continuously over a lifetime (70 years) to a concentration of 1 microgram per cubic meter ($\mu g/m^3$) of the pollutant in the air the individual breathes. For cadmium, the unit risk factor is estimated to be 1.8×10^{-3} or 1.8 chances in 1,000.

Estimates of public exposure are derived using dispersion models and census data contained in EPA's Human Exposure Model (HEM). Dispersion models are used to predict concentrations of a pollutant in the ambient air at varying distances in all directions within a 50 kilometer radius from a stationary emission source. By inputting emission estimates and stack parameters such as height, gas velocity, gas temperature, and diameter, the model is able to predict ambient pollutant concentrations around the plant. By combining the predicted ambient concentrations with population data, both the number of people exposed and their levels of exposure can be calculated.

B. Results

Emission estimates were generated for each of the sources at all of the plants in both categories. Each source at each plant was modeled separately and generated its own maximum individual risk (expressed as a probability for an individual) and aggregate risk (expressed as statistical cases per year). The risks from all sources at a particular plant were then summed to provide maximum individual risk and aggregate risk for that plant. Table 2 summarizes the risk analysis results for the pigment and stabilizer plants.

IV. POTENTIAL FOR IMPROVED CONTROL

A. Pigment Manufacturing

As shown in Table 2, only one of the four pigment plants has a maximum lifetime risk in excess of 1×10^{-4}, and none of the plants has an annual incidence in excess of 0.01 case/year. Each source at each plant was evaluated on the basis of the actual outlet particulate matter concentration to determine the potential for improved control. If the existing particulate matter emissions were less than or equal to 0.005 gr/dscf (the lowest particulate matter standard that would likely be technically enforceable for this source category) or if the source was already equipped with a baghouse, no further evaluation of improved control was performed because baghouses are considered BDT. If, however, the particulate matter emissions were greater than 0.005 gr/dscf, control options for achieving this level were developed and control costs were calculated. Based on this analysis, two plants showed potential for improved control. Control options evaluated included installing baghouses

TABLE 2. SUMMARY OF MODELING RESULTS FOR PIGMENT AND STABILIZER PLANTS

Category/plant	Cancer incidence, case/yr	Maximum individual risk, $x10^{-}$
Pigment Manufacturing		
Ciba-Geigy	0.0096	3.34
H. Kohnstamm	0.0044	0.18
Harshaw/Filtrol	0.0046	0.56
SCM Corp.	0.0024	0.49
Total	0.021	
Stabilizer Manufacturing		
Ferro Corp.	0.0001	0.0497
Interstab Chemicals	0.0004	0.0317
R. T. Vanderbilt	0.0002	0.131
Synthetic Products	0.0018	0.383
Witco Chemical Corp.	0.0102	0.230
Total	0.013	

for currently uncontrolled sources and high-energy venturi scrubbers for sources currently controlled by low-energy scrubbers for sulfur dioxide control. Table 3 presents the emission and risk reductions attributable to improved control at the two plants.

It was assumed that the baghouses currently in use are designed properly and are well operated and maintained. However, there are two bag-type collectors used at Harshaw/Filtrol for which emissions exceed greatly 0.005 gr/dscf (0.5 and 0.8 gr/dscf based on a mass balance around each collector). These collectors are used only when pigments are being transferred between tote bins, and, therefore, annual cadmium emissions and resulting risks are low (less than 6 kg/yr each and less than 4×10^{-5}, respectively). The incidence from these two sources is 0.0001 case/yr. Because of the small amount of emissions (6 percent of the total plant emissions) and the low risk and incidence, improved controls were not evaluated for these two sources.

The Calvert venturi scrubber model was used to evaluate cases where a higher energy wet scrubber was required to achieve an emission level of 0.005 gr/dscf. This computer model predicts the pressure drop needed to achieve a certain particulate removal efficiency given the gas velocity in the venturi throat, the mean particle size, and the inlet loading. These parameters were developed from the background information collected during the study and from specific information provided by the plants about the gas stream being modeled. The scrubber control options presented in Table 3 reflects the results of the modeling effort to determine the pressure drop needed to attain an emission rate of 0.005 gr/dscf.

The total emission reduction possible for the two plants is: 0.31 Mg/yr for Ciba-Geigy and 0.031 Mg/yr for SCM Corporation. As shown in Table 3, the capital costs of achieving this emission reduction range from $56,000 at SCM Corporation to $677,600 for Ciba-Geigy. The annualized costs of operating the improved control equipment range from $22,000 to $154,000. The cost/benefit ratios range from $18,300,000/life to $44,000,000/life including a particulate removal credit of $3,300/Mg.

B. Stabilizer Manufacturing

As shown in Table 2, the results of the risk analysis indicated that one plant, Witco Chemical Corporation, had an annual cancer incidence of approximately 0.01 case/yr. Additional evaluation revealed that none of

TABLE 3. RISK, INCIDENCE, AND COSTS FOR EACH CONTROL OPTION AT PIGMENT PLANTS

Plant/source	Existing control, emissions	Improved control option	Emission reduction, kg Cd/yr	Incidence reduction, case/yr	Capital cost, $	Annual cost, $	$/life for improved control[a]	$/Mg emission reduction
Ciba-Geigy, Glens Falls, N.Y.								
Calciner load and dump hoods	Uncontrolled, 0.019 gr/dscf each	Baghouse for hoods (99.5% efficient)	312	0.0025	560,000	110,000	44,000,000	353,000
Calcining	Impingement WS (pressure drop=6 in.), 0.0071 gr/dscf	Venturi WS on calciners (pressure drop=10 in.), 0.005 gr/dscf	110	0.0010	117,600	41,800	41,800,000	373,000
		BH on hoods and venturi WS on calciners	422	0.0035	677,600	151,800	43,400,000	360,000
		Venturi WS (pressure drop=40 in.) to control hoods and calciners.	422	≤0.0035	336,000	154,000	44,000,000	365,000
SCM Corp., Baltimore, Md.								
Red calcining	Venturi WS (pressure drop= 30 in.), 0.0091 gr/dscf	New venturi WS on each (pressure drop= 40 in.), 0.005 gr/dscf	31	0.0011	56,000	22,000	18,300,000	710,000
Yellow calcining	Venturi WS (pressure drop= 20 in.), 0.04 gr/dscf			0.0001				

[a]Includes a particulate recovery credit of $3,300/Mg.

the sources at this plant had the potential for improved control (i.e., all sources were already controlled by well-designed and -operated baghouses that are considered BDT and/or had particulate matter emissions less than or equal to 0.005 gr/dscf). Therefore, improvements in existing control that are feasible for the stabilizer source category would not significantly reduce the risk from cadmium.

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